

TOXICITY OF 2,4-D IN CALIFORNIA SOILS¹

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Studies with 2,4-D in soils have shown that, like other herbicides, it is toxic to plants when absorbed through the roots. Because of a wide variation in plant tolerance, chemicals of this type may be used selectively to kill weeds without appreciably damaging crops. And, because of their extreme toxicity, such differential action can be obtained using less than one pound of chemical per acre.

SUMMARY OF PREVIOUS RESEARCH

The work of Slade, Templeman, and Sexton (1945)² in England proved conclusively that 2,4-D and many other compounds having similar properties will kill weeds when applied directly to the soil. Leaching tests by Nutman, Thornton, and Quastel (1945) proved that 2,4-D was not completely removed from a Rothemsted soil by 5.6 inches of water.

In contrast to the British work, studies in this country have stressed the use of 2,4-D compounds as sprays against perennial weeds, and during the early period of investigation effects through the soil were overlooked or neglected. Many of the original containers which were used to distribute 2,4-D to users were labeled "Will not sterilize the soil." The fallacy of such labeling has been pointed out (Crafts, 1945).

Studies by De Rose at Camp Detrick (1946) confirmed the toxicity of 2,4-D in soils and showed that it could be removed by leaching. Hanks (1946) observed that leaching removed 2,4-D from limed as well as unlimed soils. An alkaline soil retained the toxicant longer than neutral or acid soils.

Taylor (1947) found 2,4-D to persist in the field seven weeks or more following treatment at four pounds per acre. Pretreatment with 2,4-D to control weeds resulted in stimulation of growth of beans and corn to values above those of control cultures. Kries (1947) found 2,4-D to persist for 18 weeks in dry soil but to decompose during four weeks of cropping in the greenhouse.

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² See "Literature Cited" for complete data on citations referred to in text by name of author and date of publication.

Lime delayed decomposition. Some stimulation was noted where 2,4-D had decomposed. Different plants showed varying sensitivity to 2,4-D toxicity.

Weaver (1947) studied the adsorption of 2,4-D by cation and anion exchangers. Cation exchangers in the hydrogen cycle adsorbed much 2,4-D and its salts. In the sodium- or calcium-saturated condition they adsorbed little or no 2,4-D. Anion exchangers adsorbed much 2,4-D and its salts, but not always in equal amounts. Adsorbed 2,4-D was less available to plants than that in true solution.

PURPOSE OF PRESENT STUDIES

Studies on 2,4-D in soils in California were initiated to determine:

1. The residual effects of 2,4-D in soils
2. The possible use of 2,4-D as a selective temporary soil sterilant under the semiarid conditions prevailing in California
3. The possible use of 2,4-D as a soil sterilant in nontilled areas.

Work on 2,4-D toxicity in soils began in April, 1945, and one short publication (Crafts, 1946) has presented some of the early results. The present studies involve toxicity tests in eight soils, percolation tests in five soils, and leaching tests in three soils, all soils from series agriculturally important to California. While these studies in the greenhouse were in progress, field trials (Harvey and Crafts, 1945) and many commercial applications of 2,4-D were under observation.

MATERIALS AND METHODS

The soils used in the greenhouse were stocks of air-dry surface samples that had been collected in the field and assembled in Davis several years ago. They had been pulverized and screened at the time of collection.

The toxicity tests were conducted by a method described in several previous papers (Crafts, 1935, 1936, 1945). Several series of pot cultures, each series containing 10 cultures, were grown in the greenhouse in No. 2 cans. Three test plants were used: Kanota oats, sunflowers, and Alaska field peas. The series of oat cultures contained the following concentrations of 2,4-D: 0.0, 0.1, 0.2, 0.4, 0.8, 1.6, 3.2, 6.4, 12.8, and 25.6 p.p.m. in the air-dry soil. The sunflower and pea cultures contained 2,4-D at one tenth the above concentrations. The crops were grown 30 days from planting and then cut off at ground level and the heights and fresh weights measured.

The soils used were Aiken clay loam, Egbert loam, Hanford fine sandy loam, Sierra fine sandy loam, Stockton adobe clay, Yolo fine sandy loam, Yolo clay loam, and Yolo adobe clay. Each culture contained 500 grams of soil.

In setting up the experiments the necessary amount of 2,4-D was measured from a stock solution, diluted to a total volume sufficient to bring the soil of the culture to field capacity, and added to the soil. The cans were not perforated and all watering (tap water) was done by weight so that nothing was lost from the cans. When the first crop had been harvested the tops of the plants were returned to each culture. After drying for about 30 days the tops were removed, the soil taken out and pulverized, the tops placed in the empty can, and the soil poured in. Finally, the cultures were watered to weight and seeded. This process was repeated for each crop.

Percolation tests were conducted using celluloid soil tubes filled with air-dry soil and moistened from above through small glass pipettes adjusted to deliver about 12 drops of 2,4-D stock solution per minute. When a complete set of tubes had been moistened, each tube was laid on its side on a table and opened. The soil column was cut into eleven equal portions; each portion was mixed, placed in a No. 2 can, and seeded. The test plants used were oats and peas, and the concentrations are given in the tables containing the crop data. These tests were designed to study retention of 2,4-D by soils.

Leaching tests were run by moistening soil tubes as explained above and then leaching each with a predetermined volume of distilled water. The leached columns were divided and seeded and the crop yield after 30 days used to measure 2,4-D toxicity in the soils.

TABLE 1

WEIGHTS (IN GRAMS) OF KANOTA OAT PLANTS GROWN IN CULTURES OF EIGHT CALIFORNIA SOILS AT VARIOUS CONCENTRATIONS OF 2,4-D

(All values are averages of two replicates)

Soils	2,4-D concentrations in p.p.m.									
	0.0	0.1	0.2	0.4	0.8	1.6	3.2	6.4	12.8	25.6
Kanota oats, first run, May 4-June 4, 1945										
Aiken clay loam.....	3.9	3.3	3.5	3.4	3.5	2.9	2.2	1.8	0.9	0.6
Egbert loam.....	7.5	7.9	7.0	6.9	7.0	7.4	6.5	5.0	2.7	1.4
Hanford fine sandy loam.....	6.9	7.0	6.7	6.3	6.5	5.5	4.2	1.9	1.0	0.5
Sierra fine sandy loam.....	3.4	3.1	2.9	3.0	3.2	3.4	3.1	2.7	2.3	1.9
Stockton adobe clay.....	2.8	3.1	3.0	2.8	3.1	2.4	2.0	1.6	0.9	0.7
Yolo fine sandy loam.....	5.3	5.1	5.0	5.1	4.7	2.8	1.6	0.7	0.4	0.3
Yolo clay loam.....	10.7	12.1	12.3	11.6	11.3	11.8	11.7	9.2	3.3	0.6
Yolo adobe clay.....	7.8	7.9	6.9	6.8	6.4	5.9	4.4	2.3	0.7	0.4
Kanota oats, second run, July 7-Aug. 7, 1945										
Aiken clay loam.....	3.2	3.2	2.5	3.2	2.9	3.1	3.2	3.3	2.4	2.9
Egbert loam.....	7.8	8.1	7.5	7.5	7.9	7.7	8.1	7.6	8.2	8.3
Hanford fine sandy loam.....	4.6	4.7	4.0	3.8	4.0	3.3	4.3	4.0	3.4	3.9
Sierra fine sandy loam.....	4.1	4.1	3.3	3.7	3.7	3.4	3.5	3.7	4.2	3.8
Stockton adobe clay.....	6.3	5.6	5.8	6.0	6.0	6.3	6.6	6.5	6.7	7.2
Yolo fine sandy loam.....	2.5	2.6	2.6	2.8	2.8	3.7	3.7	3.8	1.5	0.6
Yolo clay loam.....	6.4	7.1	8.1	7.9	7.4	7.9	8.4	8.7	8.6	3.8
Yolo adobe clay.....	4.3	4.6	4.6	4.7	5.2	5.4	6.2	7.1	6.3	1.1
Kanota oats, third run, Oct. 5-Nov. 5, 1945										
Aiken clay loam.....	3.7	3.3	2.6	3.1	2.8	3.4	3.1	4.2	3.8	3.8
Egbert loam.....	6.3	7.2	5.7	5.7	5.9	5.9	6.3	6.1	6.8	6.9
Hanford fine sandy loam.....	5.9	5.2	5.7	6.0	5.6	5.7	5.7	6.0	6.2	6.3
Sierra fine sandy loam.....	3.4	3.5	3.2	3.3	3.3	3.1	3.6	3.6	3.7	4.4
Stockton adobe clay.....	3.5	3.6	4.1	4.1	3.7	4.2	3.5	3.9	4.8	4.7
Yolo fine sandy loam.....	1.5	2.1	1.6	1.9	2.3	2.5	2.8	3.2	3.1	3.3
Yolo clay loam.....	4.5	5.2	5.5	5.7	5.2	6.0	5.2	6.8	8.4	10.2
Yolo adobe clay.....	3.2	3.0	3.2	3.0	3.5	3.8	4.5	4.5	6.1	7.5

RESULTS

Toxicity. Tables 1, 2, 3, and 4 report the crop yields on the toxicity tests and figures 1 to 8 illustrate the first run data. Each series was duplicated and the values given are the averages of the two replicates. Three runs were made using oats; a final run on the same cultures was made using peas (table 4). In addition, high concentration cultures were added at the end of the first run to the series in Egbert loam and Stockton adobe clay. The results on these are included in table 4.

A study of the graphs shows that 2,4-D toxicity was high and approximately the same in Hanford fine sandy loam, Yolo fine sandy loam, and Yolo adobe clay. Next in line was Yolo clay loam, with somewhat lower toxicity, followed by Sierra fine sandy loam, Aiken clay loam, Egbert loam, and finally, Stockton

TABLE 2
WEIGHTS (IN GRAMS) OF SUNFLOWERS GROWN IN CULTURES OF EIGHT CALIFORNIA SOILS AT VARIOUS CONCENTRATIONS OF 2,4-D
(All values are averages of two replicates)

Soils	2,4-D concentrations in p.p.m.									
	0.00	0.01	0.02	0.04	0.08	0.16	0.32	0.64	1.28	2.56
Sunflowers, first run, May 4-June 4, 1945										
Aiken clay loam.....	9.5	9.3	10.2	10.3	9.8	9.9	8.6	7.6	6.5	5.6
Egbert loam.....	16.8	16.3	15.8	17.2	18.5	16.7	15.3	18.0	14.3	14.1
Hanford fine sandy loam.....	12.0	13.0	14.1	13.1	15.0	13.3	10.8	7.0	2.6	1.5
Sierra fine sandy loam....	8.1	7.3	7.9	8.2	7.6	7.6	7.3	8.4	6.5	6.3
Stockton adobe clay.....	10.2	11.0	10.4	12.1	11.5	11.5	9.4	8.7	9.7	7.3
Yolo fine sandy loam.....	11.6	11.8	11.9	11.2	11.2	10.4	9.2	5.3	0.6	0.0
Yolo clay loam.....	25.9	25.7	26.4	27.5	26.5	26.5	23.7	23.8	21.7	15.9
Yolo adobe clay.....	17.9	18.1	16.4	15.8	15.2	16.1	11.0	8.2	2.7	0.5
Sunflowers, second run, July 7-Aug. 7, 1945										
Aiken clay loam.....	7.1	7.0	6.4	7.0	7.1	7.7	6.8	7.6	6.6	8.0
Egbert loam.....	14.5	16.2	15.6	14.4	17.8	14.5	15.2	15.0	14.6	15.3
Hanford fine sandy loam.....	8.8	8.4	8.1	8.2	8.1	8.4	8.1	9.1	6.4	8.7
Sierra fine sandy loam....	7.7	7.5	6.5	6.5	7.1	6.4	7.7	6.2	6.4	7.0
Stockton adobe clay.....	11.5	11.9	11.6	13.4	12.0	12.7	13.6	14.2	11.1	12.2
Yolo fine sandy loam.....	6.7	7.0	7.6	7.4	7.8	7.1	7.9	8.3	8.6	8.6
Yolo clay loam.....	14.7	15.3	17.4	16.4	17.2	17.1	15.3	17.4	17.5	17.1
Yolo adobe clay.....	13.4	13.5	12.3	12.3	12.7	12.8	14.1	13.7	14.5	14.4
Sunflowers, third run, Oct. 5-Nov. 4, 1945										
Aiken clay loam.....	11.4	8.5	10.4	11.3	13.5	13.6	11.4	10.8	11.4	10.2
Egbert loam.....	18.5	17.9	16.5	18.1	18.6	15.2	17.4	15.6	14.3	15.0
Hanford fine sandy loam.....	13.0	12.4	12.7	12.1	12.9	13.8	15.6	14.5	12.3	13.4
Sierra fine sandy loam....	10.1	10.0	9.6	9.4	8.2	10.3	9.7	9.9	9.5	9.8
Stockton adobe clay.....	11.2	12.6	10.4	11.3	12.8	11.1	11.7	11.7	10.8	11.4
Yolo fine sandy loam.....	9.8	8.8	8.5	8.1	8.9	8.0	8.5	8.7	9.4	7.7
Yolo clay loam.....	14.2	13.7	16.0	14.6	16.1	15.7	15.4	16.7	15.9	19.5
Yolo adobe clay.....	13.8	13.7	14.1	12.9	14.5	13.5	14.6	14.6	13.1	13.8

adobe clay. There seems to be no simple relation between toxicity and soil characteristics among these eight soils. Except for the position of Yolo adobe clay in this line-up, a tendency toward correlation of toxicity with textural grade is discernible, toxicity being high in light, sandy soils and lower with decreasing particle size. The evidence given later that 2,4-D is retained by soils against the leaching action of moving water supports this view. On the other hand, Yolo adobe clay is an obvious exception to this rule, and no explanation is available. Because the Yolo soils are recent alluvial in origin, the adobe clay is probably water-separated instead of weathered to a clay state. Hence, though Yolo adobe clay is composed of very fine particles and displays adobe characteristics, it may be lower in actual colloid content than a soil like Stockton adobe clay. Yolo adobe clay showed anomalous behavior in arsenic studies also (Crafts and Rosenfels, 1939; Rosenfels and Crafts, 1939).

TABLE 3

WEIGHTS (IN GRAMS) OF ALASKA FIELD PEAS GROWN IN CULTURES OF EIGHT CALIFORNIA SOILS AT VARIOUS CONCENTRATIONS OF 2,4-D

(All values are averages of two replicates)

Soils	2,4-D concentrations in p.p.m.									
	0.00	0.01	0.02	0.04	0.08	0.16	0.32	0.64	1.28	2.56
Alaska field peas, first run, May 4-June 4, 1945										
Aiken clay loam.....	6.0	6.2	5.9	6.7	6.5	6.4	6.2	4.9	3.1	1.1
Egbert loam.....	10.1	9.9	9.3	9.8	9.2	9.7	8.9	8.4	7.5	3.9
Hanford fine sandy loam.....	7.5	7.6	7.0	7.2	7.7	6.3	4.3	1.1	0.1	0.0
Sierra fine sandy loam.....	5.3	5.6	5.5	5.8	6.2	6.2	5.0	3.8	1.5	0.2
Stockton adobe clay.....	7.9	8.5	7.3	9.4	8.2	8.1	7.2	8.6	7.7	5.8
Yolo fine sandy loam.....	7.4	7.2	7.3	6.9	7.2	6.5	3.8	0.6	0.0	0.0
Yolo clay loam.....	13.4	12.3	10.2	12.3	13.0	11.9	10.0	2.2	1.3	0.0
Yolo adobe clay.....	10.3	8.6	8.7	7.8	7.2	7.4	5.9	2.5	0.1	0.0
Alaska field peas, second run, July 7-Aug. 7, 1945										
Aiken clay loam.....	2.9	3.5	2.9	3.5	3.5	3.5	4.0	3.3	3.6	3.8
Egbert loam.....	7.8	6.9	6.6	6.7	6.1	7.3	6.9	6.0	6.7	7.2
Hanford fine sandy loam.....	3.1	3.5	3.2	2.9	3.9	2.5	3.3	3.8	3.6	3.4
Sierra fine sandy loam.....	4.9	4.3	4.2	4.3	4.7	4.0	3.6	4.2	4.8	5.1
Stockton adobe clay.....	7.9	6.9	7.5	8.5	7.2	8.1	7.5	8.1	7.5	7.1
Yolo fine sandy loam.....	3.1	3.1	4.5	4.0	5.0	4.1	4.1	3.9	4.0	3.8
Yolo clay loam.....	4.8	4.9	4.5	5.0	5.1	5.1	5.2	5.2	4.7	5.4
Yolo adobe clay.....	6.7	6.4	6.9	6.6	6.4	6.3	6.5	6.3	6.1	6.3
Alaska field peas, third run, Oct. 5-Nov. 5, 1945										
Aiken clay loam.....	4.5	5.6	4.9	4.7	5.6	5.9	6.1	6.0	5.9	5.8
Egbert loam.....	9.8	8.7	7.4	6.7	8.7	7.7	7.1	5.7	4.8	6.5
Hanford fine sandy loam.....	7.2	7.0	5.7	5.8	6.2	5.4	3.2	6.0	5.0	9.5
Sierra fine sandy loam.....	6.2	5.5	6.1	6.2	7.0	6.3	6.1	6.2	6.0	5.9
Stockton adobe clay.....	8.9	8.1	8.7	7.0	9.3	8.8	8.3	7.9	9.5	8.4
Yolo fine sandy loam.....	3.2	3.6	3.3	3.2	3.9	4.0	3.8	3.8	3.5	3.4
Yolo clay loam.....	4.8	6.0	6.6	7.4	6.0	6.0	6.0	7.2	7.2	6.8
Yolo adobe clay.....	8.2	5.0	6.7	5.0	5.7	8.4	5.6	6.7	8.1	6.7

The additional concentrations added to the series in Egbert loam and Stockton adobe clay at the end of the first run proved that sufficiently high concentrations of 2,4-D will render even these soils sterile. However, by the third and fourth runs this additional chemical had decomposed in the soil.

TABLE 4

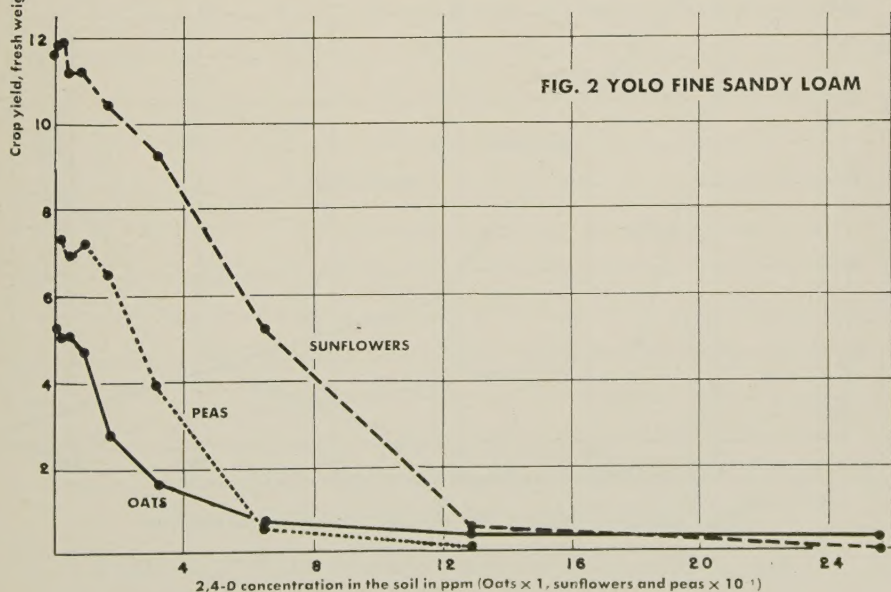
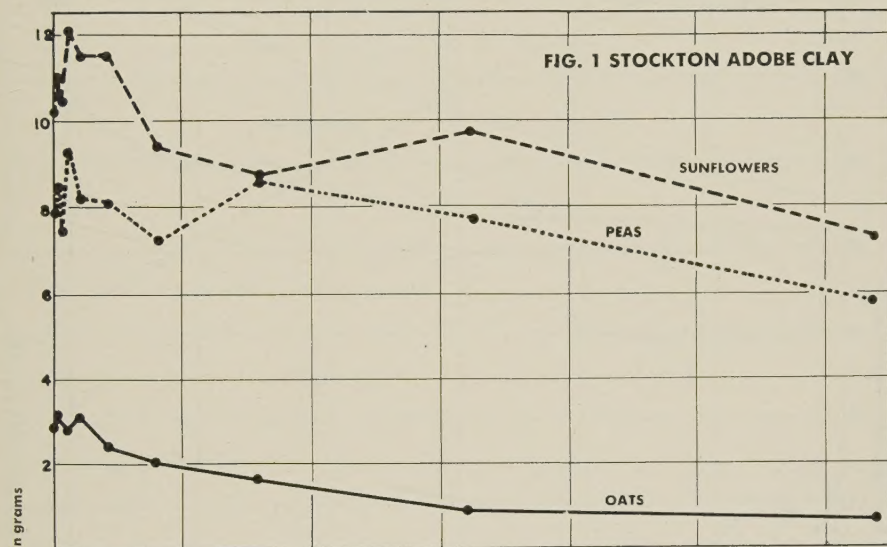
WEIGHTS (IN GRAMS) OF ALASKA FIELD PEAS GROWN IN CULTURES OF EIGHT CALIFORNIA SOILS AT CONCENTRATIONS OF 2,4-D PREVIOUSLY SOWN TO OATS; ALSO HIGH CONCENTRATION RUNS ON OAT, SUNFLOWER, AND PEA PLANTS

Soils	2,4-D concentrations in p.p.m.									
	0.0	0.1	0.2	0.4	0.8	1.6	3.2	6.4	12.8	25.6
Peas, fourth run, Dec. 23, 1945-Jan. 23, 1946										
Aiken clay loam.....	5.8	5.5	5.3	6.3	4.9	5.9	5.7	5.0	4.9	5.1
Egbert loam.....	9.7	10.2	9.7	10.1	8.9	8.5	8.7	9.5	11.5	9.7
Hanford fine sandy loam.....	6.2	7.0	5.8	6.0	6.4	6.7	7.7	7.1	6.9	7.3
Sierra fine sandy loam.....	6.6	6.8	6.7	7.8	7.4	7.3	6.6	8.0	7.3	7.5
Stockton adobe clay.....	8.9	10.1	9.1	10.8	8.5	10.1	10.7	10.5	10.0	8.5
Yolo fine sandy loam.....	6.0	5.8	5.3	4.5	4.8	3.9	5.8	4.9	6.0	5.5
Yolo clay loam.....
Yolo adobe clay.....	7.7	7.6	5.2	5.9	6.6	6.0	6.7	6.2	7.0	7.4

2,4-D concentrations in p.p.m.							
	51.2	102.4	5.12	10.24	5.12	10.24	
	Oats		Sunflowers		Peas		
Egbert loam second run.....	0.4	0.2	14.2	13.1	6.0	5.6	
Egbert loam third run.....	6.5	6.6	15.9	16.7	9.4	7.6	
	Peas						
Egbert loam fourth run.....	9.9	5.6	

2,4-D concentrations in p.p.m.								
	51.2	102.4	204.8	5.12	10.24	20.48	5.12	10.24
	Oats			Sunflowers			Peas	
	2.1			14.2			7.0	
	6.8			12.9			3.2	
	Peas							
Stockton adobe clay second run.....	2.1	0.8	0.5	14.2	13.9	6.6	7.0	5.9
Stockton adobe clay third run.....	6.8	7.7	8.0	12.9	12.9	14.4	3.2	4.4
Stockton adobe clay fourth run.....	9.8	8.7	8.0

Examination of the data for the second and third runs proved that in practically all cases the chemical had so decomposed that little toxicity was left. In all cases by the third run cultures somewhere along in the series were heavier than the untreated checks. In the heavy soils some crops were up to twice or more the weight of the checks, indicating definite stimulation. Such stimulation has been noted in a number of studies on such herbicides as borax,



Figs. 1 and 2. Toxicity of 2,4-D to indicator plants in 8 California soils.

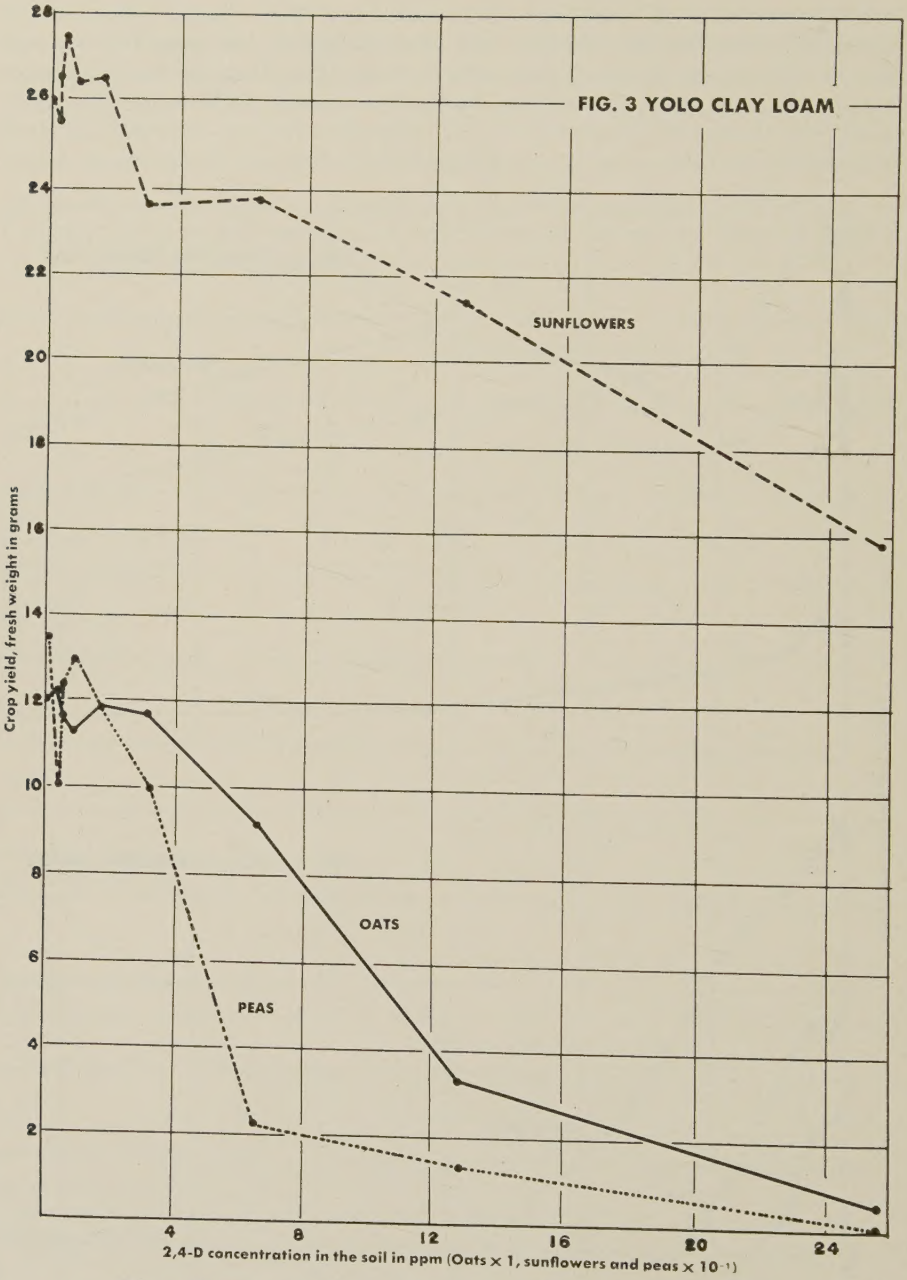
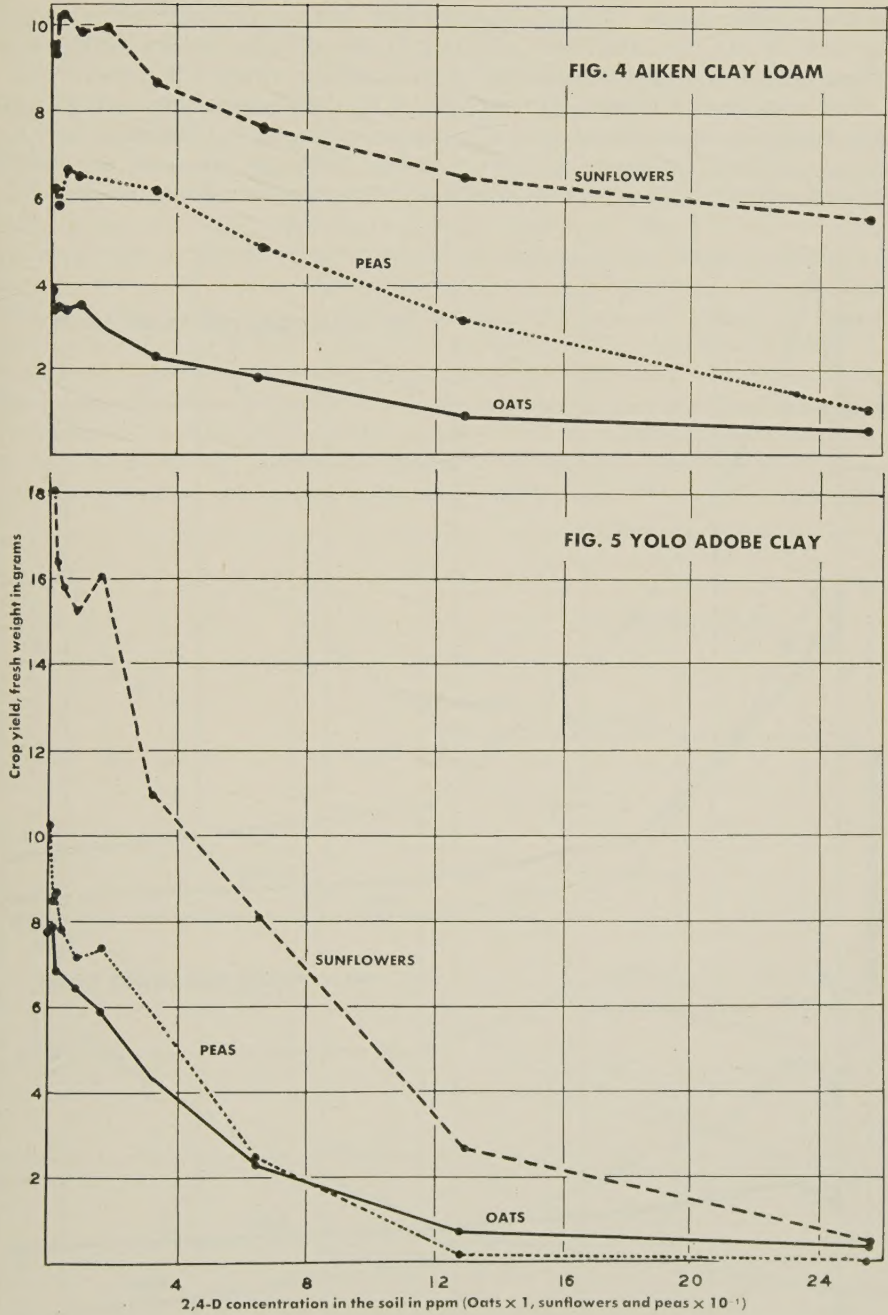


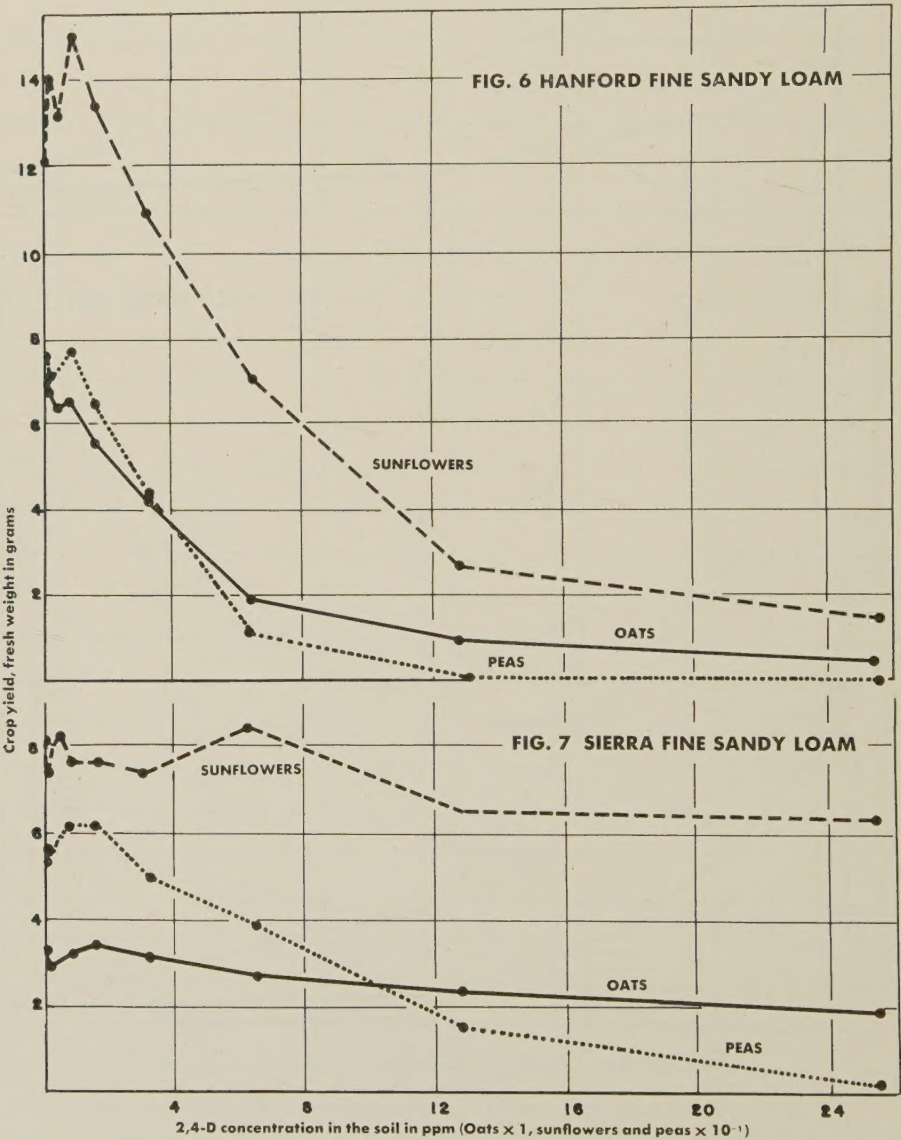
Fig. 3. Toxicity of 2,4-D to indicator plants in 8 California soils.



Figs. 4 and 5. Toxicity of 2,4-D to indicator plants in 8 California soils.

chlorate, thiocyanate, ammate, and phenols, but only in soils where larger amounts of chemical have been involved. Hanks (1946), Taylor (1947), and Kries (1947) all noted stimulation in their studies with 2,4-D.

The consistent differences in toxicity of 2,4-D between oats and the two broad-leaved crops indicate the natural range of biological tolerance to toxic chemicals found wherever plants of widely differing character are tested against a single toxic substance. These differences are the basis for the selec-



Figs. 6 and 7. Toxicity of 2,4-D to indicator plants in 8 California soils.

tive action of 2,4-D and other chemicals on weeds in cereals when treated through the soil (Slade, Templeman and Sexton, 1945).

Percolation. Results of percolation tests illustrated by figures 9 and 10 prove that 2,4-D is retained in soils, behaving about like borax in that respect.

Inspection of the graphs on oats shows most of the chemical retained in the top four fractions in Hanford sandy loam, in the top six in Yolo clay loam, in the top six in Stockton adobe clay with some in the seventh and eighth fractions, in the top eight fractions in Fresno loam and in the top nine in Yolo fine sandy loam. As the concentration was increased the chemical tended to occupy more soil, this tendency being stronger in Hanford, Fresno, and Stockton soils than in Yolo. Retention of 2,4-D does not follow any fixed pattern of behavior as does arsenic but varies in such a way that neither textural grade nor parent material gives any clear clue to the factors involved. The retention shown indicates that 2,4-D residues in soils will tend to remain concentrated in surface layers and will not leach as readily as chemicals such as chlorate or nitrate. Results of retention indicated by peas are fairly comparable with those where oats were used, particularly since much lower dos-

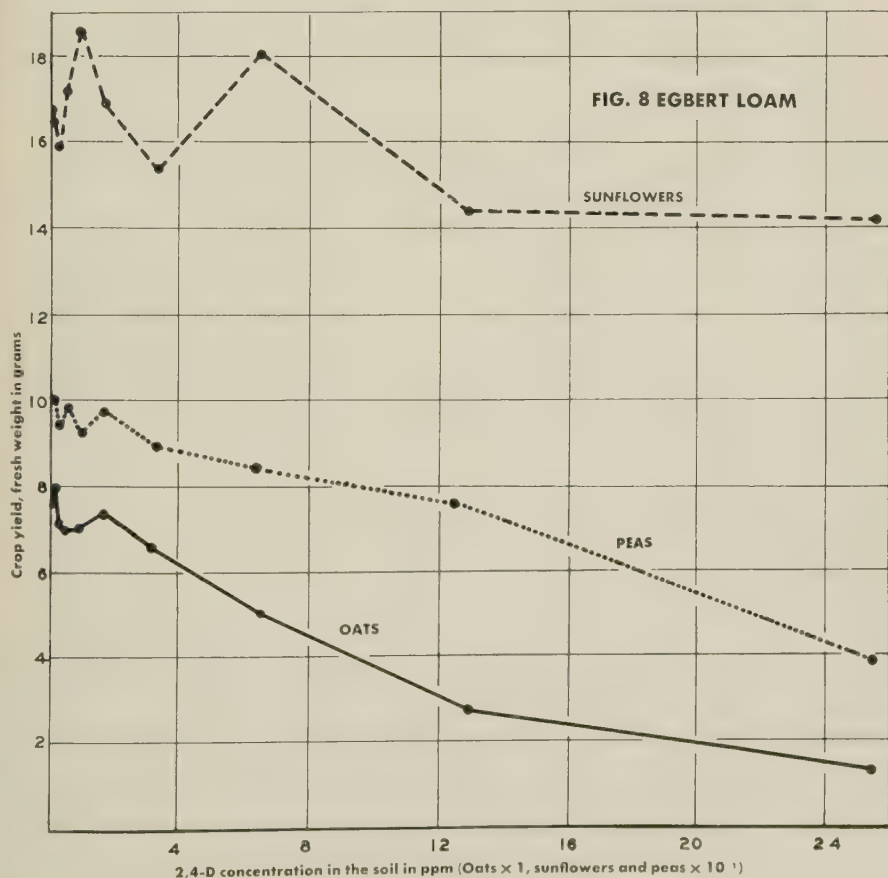


Fig. 8. Toxicity of 2,4-D to indicator plants in 8 California soils.

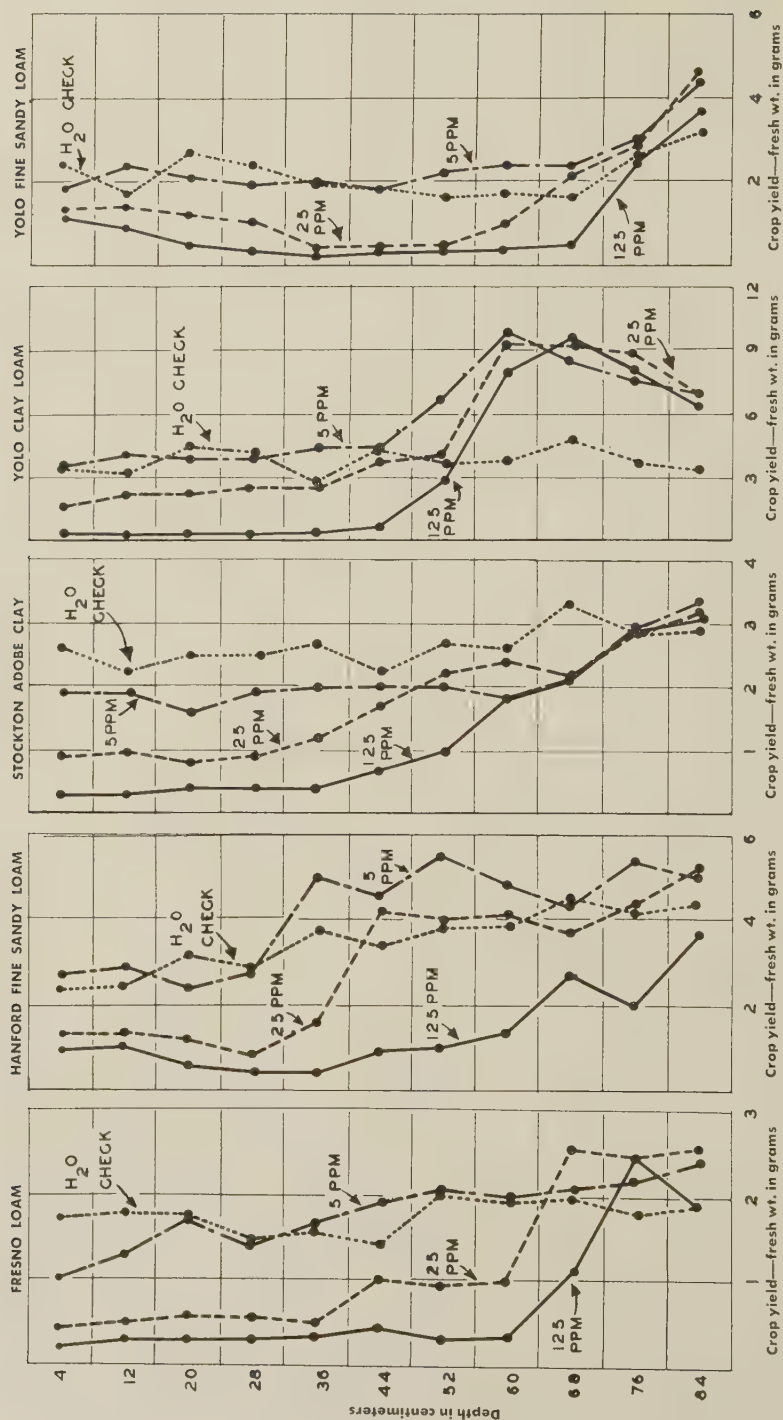


Fig. 9. Penetration of 2,4-D into 5 California soils as shown by yield of oats.

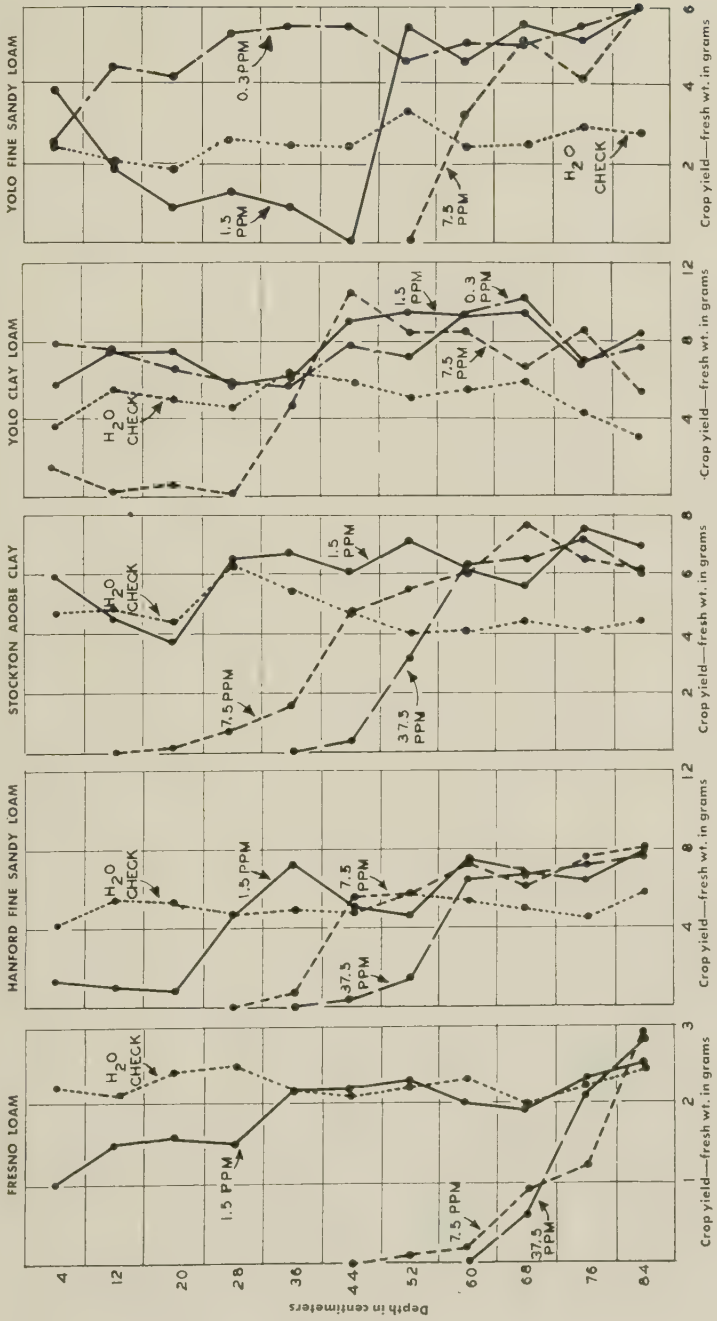


Fig. 10. Penetration of 2,4-D into 5 California soils as shown by yield of peas.

ages caused injury. The initial concentrations were 0.3, 1.5, and 7.5 p.p.m. and the curves for Yolo fine sandy loam illustrate these. Because the 0.3 p.p.m. showed no toxicity the remaining tests were run using 37.5 p.p.m. and leaving off 0.3 p.p.m.

Leaching. Using 125 p.p.m. as the initial moistening concentration and oats as indicator plants, leaching tests were run in Stockton adobe clay, Yolo fine sandy loam, and Yolo clay loam. Results are illustrated in figure 11. In Stockton adobe clay the chemical was retained from the initial moistening solution in the top eight fractions. Ten cm of water lowered the concentration slightly but did not displace the chemical from the top of the column. This application did lower the bottom of the region of concentration into the ninth and tenth fractions. Twenty cm lowered the concentration appreciably in the top two fractions and probably took a bit of the chemical into the bottom fraction. Forty cm reduced the concentration even more in the top two fractions and displaced the concentrated layer into the bottom fraction. Eighty cm lowered the concentration in the third and fourth fractions, 160 lowered it in the nine top fractions, and 320 washed it completely from all but the eleventh fraction.

Leaching displaced the chemical downward somewhat more readily in Yolo fine sandy loam, but in Yolo clay loam the original percolation left the chemical more firmly tied in the soil, leaching was a bit less effective, and even 320 cm left appreciable concentrations in the tenth and eleventh fractions.

If the curves of figures 9 and 10 are carefully examined it will be found that in several cases crop yields are greater on soils moistened with solutions that originally contained 2,4-D than they are on soils moistened with water. This is evidence again that very low concentrations of 2,4-D are stimulating. This aspect of the use of growth regulators should be thoroughly studied; it indicates a possible use of these materials as a supplement to fertilizer application.

DISCUSSION

Results of the experiments reported here, plus observations in the field, have led us to the following conclusions:

1. Under California conditions residual toxicity of 2,4-D following spray application is sufficient to cause injury to subsequent crops, the extent of injury depending on temperature, moisture, and soil reaction.
2. In semiarid western states, spraying 2,4-D on foliage gives better and safer weed control than application direct to the soil.
3. Where winter rainfall does not exceed 10 inches, 2,4-D might be used as a permanent soil sterilant, but in general other chemicals are preferable.

Results in the field have proved that 2,4-D will not decompose in soils of the semiarid western states as readily as it does in regions of summer rains. This was predicted from the first preliminary runs in preparation for the studies reported here (Crafts, 1946). Two years' field experience (Harvey and Crafts, 1945) has confirmed the prediction and the results reported here explain the reasons.

Apparently 2,4-D remains active in soils after its application for a period of time depending largely upon temperature and moisture. In practically all cases of injury in the field the soils have been dry while they were warm.

Moistening by rainfall during the cold winter period did not result in sufficient decomposition to render the soil free of toxicity. Many losses have occurred from spring planting of vegetable varieties on soils sprayed coincidental with weed control during the previous fall.

In the experiments reported here, toxicity was sufficient to reduce growth during the initial cropping period in most soils. By the second crop little toxicity remained. By the third crop, stimulation was evident in many instances. These soils were kept moist during crop growth, and were warm because the greenhouse was heated.

In addition to temperature and moisture, soil reaction evidently affects the residual toxicity of 2,4-D, breakdown being slower in neutral and alkaline soils than in acid ones. Furthermore, an alkaline reaction brings about ionization of 2,4-D producing anions of the active particle. These anions, because of their negative charge, would not readily enter bacteria or fungi, and would not tend to adsorb on soil colloids. They could be taken up by plant roots, which are highly specialized for absorbing ions, and their presence in the plant would result in injury (Crafts, 1948b). These facts help to explain the slow breakdown and high residual toxicity of 2,4-D observed so often in the field.

Although the small number and wide variety of soils tested by percolation

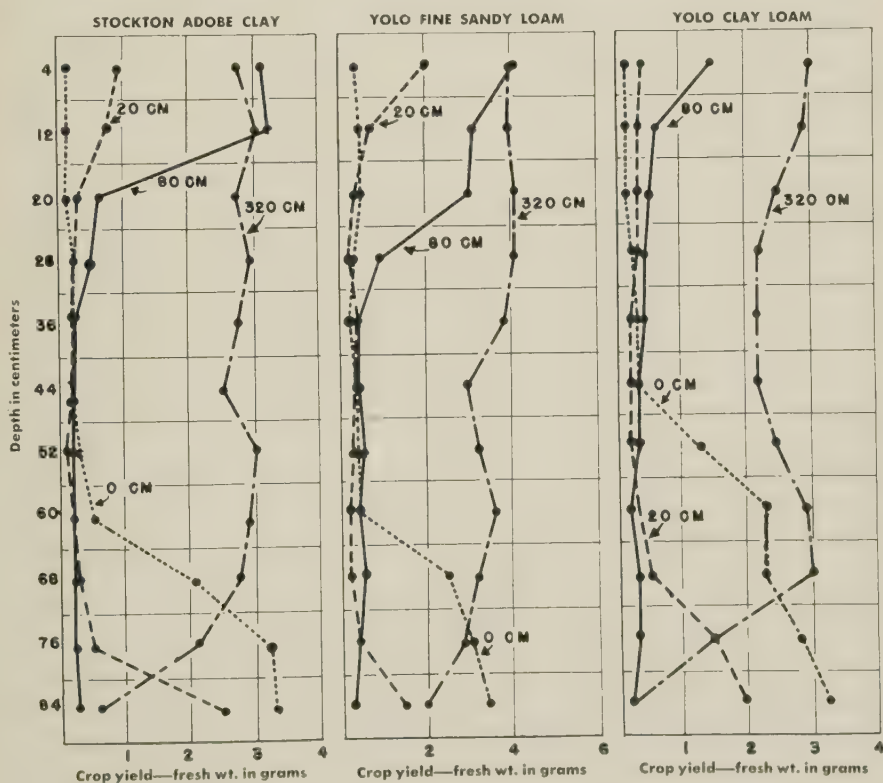


Fig. 11. Leaching of 2,4-D from 3 California soils as shown by yield of peas.

led to no obvious relations between 2,4-D retention and soil properties, the experiments proved that this chemical does not move freely with the moistening water but remains behind, held to the soil by binding forces of moderate strength. Weaver (1947) showed that both cation and anion exchangers hold 2,4-D. In soils this chemical is probably held by the clay colloids in such a form that at least a part of it is available to plants.

Though leaching resulted in some displacement of the chemical downward, the complete freeing of the soil of 2,4-D was not accomplished in two soil types with 320 surface centimeters. These results indicate that ridding the soil of 2,4-D under conditions where chemical breakdown does not occur may prove to be a real problem.

That the leaching and decomposition normally occurring during the winter are not sufficient under central California conditions is indicated by many field experiences. For example, one grower sprayed morning glory patches in a field in the fall, plowed 12 inches deep in the spring, prepared the seed bed, and planted onions. The crop failed to come up in the sprayed areas. Apparently the 2,4-D had been leached to a depth of about 12 inches, and was turned up to the surface with the deep plowing. Similar cases have been observed where shallow seedbed preparation was used. Seeds came up and made healthy seedlings, only to fail when the roots grew down into the zone containing the chemical.

Where 2,4-D is applied during spring or early summer, probably light irrigation during midsummer to provide a warm, moist condition will prove the most practical means of eliminating it by decomposition. Where application is made during the autumn and leaching by winter rains occurs, further leaching in the spring seems to be indicated.

The above discussion shows beyond doubt that 2,4-D residues constitute a real problem in California soils and that soil properties and precipitation determine the location and toxicity of the chemical. Leaching and decomposition are both concerned in the disappearance of the chemical from a given soil horizon, and temperature as well as moisture must be suitable if the latter is to be effective. Where decomposition cannot be depended upon, leaching is indicated when it is necessary to crop the treated land. When leaching is practiced, sufficient water must be used to carry the chemical beyond the zone of root growth of the crop or to dilute and spread it sufficiently to overcome the toxicity.

Concerning the use of 2,4-D as a selective herbicide through soil application, the experiments described above indicate the range of tolerance of one cereal crop and show the wide selectivity that may exist. They do provide a clue to the inadequacy of the method under the semiarid conditions of California, but field tests (Harvey and Crafts, 1945) were required to prove its weakness. Such tests showed that when only light rainfall occurred following application of 2,4-D to the soil, a shallow concentrated layer of the chemical surrounding the roots of the developing crop seedlings resulted in serious crippling of the plants despite the wide range of selectivity between crop and weeds. Protracted heavy rains, on the other hand, may leach the chemical so deep into the soil that weed seedlings germinating later in the season will survive and compete successfully with the crop.

Many field tests have proved the very practical nature of the spray method of applying 2,4-D, by which the foliage of the weeds is contacted directly. An estimated quarter million acres of cereal crops in California were sprayed in the spring of 1947. Weeds (principally wild mustard and radish) from the small seedling stages up to the blossoming condition were quickly killed, whereas the only injury to crops occurred either when spraying was done on very young seedling grain during the cold winter season or when grain coming out of the boot was treated. Early treatment resulted in crippling some oat and barley plants due to abnormal growth. Late treatment caused twisting of heads and failure to fill in a few instances.

These experiments with 2,4-D in soils show that this chemical can sterilize the soil against plant growth. However, 2,4-D leaches too readily and decomposes in warm, moist soils too rapidly to be of general use as a permanent soil sterilant. In regions where rainfall occurs only during the winter and does not exceed 10 inches, 2,4-D might prove useful for permanent soil sterilization, so long as the price remains in the neighborhood of 50 cents per pound. In most localities, however, chlorate, borax, or arsenic trioxide, properly applied, can better fulfill practically all requirements for permanent sterilization of soils.

A much more fertile field for the large-scale employment of 2,4-D would seem to be that of pre-emergence treatment in corn and sugar cane, and spraying for pasture and range improvement. When the critical aspects of pre-emergence treatment are appreciated, this method will undoubtedly be widely used (Crafts, 1948a). The low-volume method of applying 2,4-D which has received so much attention and has given such promising results seems applicable to programs of brush control (Barrons and Coulter, 1948) and range improvement exceeding anything that has ever been planned in the past. In such programs the residues of 2,4-D, far from inhibiting range crops, may actually stimulate grasses as they have seedlings and crop plants growing in soils where decomposition has eliminated toxicity (tables 1-4, 3rd and 4th runs).

ACKNOWLEDGMENT

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**TOXICITY OF AMMONIUM
DINITRO-O-SEC-BUTYL PHENOLATE
IN CALIFORNIA SOILS**

A. S. CRAFTS

TOXICITY OF AMMONIUM DINITRO-O-SEC-BUTYL PHENOLATE IN CALIFORNIA SOILS¹

A. S. CRAFTS

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The introduction of sodium dinitro-*o*-cresylate (Sinox) as a selective herbicide (Westgate and Raynor, 1940)² provided a great stimulus to chemical weed control. This organic dye was relatively noncorrosive, eliminating the hazards attending the use of sulfuric acid. To control the broad-leaved weeds in one acre of cereal, three pounds of the chemical in the form of one gallon of concentrate sufficed, whereas up to 100 pounds of sulfuric acid had been required. Furthermore, Sinox proved useful in flax, onions, garlic, peas, corn, and other crops not previously sprayed with selective herbicides.

THE PRINCIPLE OF ACTIVATION

Soon after the introduction of Sinox, it was found that the addition of an acid salt such as ammonium sulfate or sodium bisulfate would greatly increase its toxicity to plants. This became known as "activation," and it has become standard practice wherever Sinox solutions are used. In 1945, Crafts and Reiber gave the following chemical explanation for the enhanced toxicity of activated solutions of Sinox.

Sodium dinitro-*o*-cresylate in solution dissociates into the highly polar sodium and dinitro-*o*-cresylate ions. Though readily soluble in the polar solvent water, they are less soluble in the nonpolar waxy cuticle of the plant. Dinitro-*o*-cresol, on the other hand, is an un-ionized compound, soluble in the cuticle and hence able to enter the plant readily.

When an acid salt is added to an aqueous solution of sodium dinitro-*o*-cresylate the reaction $\text{Na}^+ + \text{DN}o\text{Cr}^- + \text{H}^+ \longrightarrow \text{HDN}o\text{Cr} + \text{Na}^+$ goes to the right, producing undissociated dinitro-*o*-cresol in the solution. This compound is rapidly absorbed by the plant through the cuticle and as its molecules leave the free solution on the leaves, more are produced by mass action so long as the hydrogen ion concentration is maintained. Many experiments indicate that this reduction in polarity, brought about by the association of the phenolic molecule, is responsible for the increased toxicity resulting from activation. The same chemical mechanism may be used to activate chlorinated phenol compounds.

Since reduction in polarity increases toxicity, another approach to the discovery of more efficient weed killers would be the use of longer side chains on the nitro- or chloro-substituted phenols. Because dinitro-*o*-cresol is more toxic than dinitrophenol, the ethyl-, propyl-, and butyl-substituted compounds should be even more toxic. Testing has proved this to be true (Crafts, 1945).

¹ Received for publication December 2, 1947.

² See "Literature Cited" for complete data on citations referred to in text by name of author and date of publication.

Toxicity increases through the butyl substitution and drops slightly with the amyl substitution, presumably because the dinitro groups become a smaller and hence less effective portion of the total molecule.

Following the discovery of the intense toxicity of dinitro-*o-sec*-butyl and amyl phenols, a number of commercial products based on these compounds appeared on the market, including Dow Contact herbicide, Dow General herbicide, Contax, Chipman General, Stauffer Weed Killer, and Sinox General. Ammonium salts are the active ingredients in Dow Selective, Sprayrite Selective, and Sinox W herbicides. Use of these weed killers, already widespread, will be greatly extended once their manifest advantages are recognized. This is particularly true in countries where hand methods of weed control are still practiced.

PURPOSES OF PRESENT STUDIES

Because the chlorinated and nitrated phenols will find extensive use in agriculture, it is important to know what effects their continued use will have on the soil. We should know:

1. The residual effects of the continued use of these materials as selective herbicides on croplands
2. The effects of accumulation where they are used as general contact herbicides
3. Their toxicity to seedlings when used as fortifying agents in pre-emergence sprays
4. Their possible function as soil sterilants in nontilled areas.

These studies involve nine successive croppings of eight soils treated with varying amounts of the ammonium salt of dinitro-*o-sec*-butyl phenol.

MATERIALS AND METHODS

The soils and methods used in these tests were the same as those described in the preceding paper (Crafts, 1948) except that no percolation and leaching experiments were performed and only Kanota oats were used as indicator plants. The soils used were Aiken clay loam, Egbert loam, Hanford fine sandy loam, Sierra fine sandy loam, Stockton adobe clay, Yolo fine sandy loam, Yolo clay loam, and Yolo adobe clay.

RESULTS

Figures 1-8 illustrate the results of our tests in terms of crop yields 30 days after planting.

Four of the soils used in these tests were employed previously in similar trials with dinitro-*o-cresol*. These were Yolo clay loam, Yolo fine sandy loam, Sierra fine sandy loam, and Stockton adobe clay. When the results (Crafts, 1945) are compared with those of the present study, it is evident that the dinitro-*o-sec*-butyl phenol is considerably more toxic than the dinitro-*o-cresol*. Furthermore, the breakdown in the soil goes on at a considerably slower rate; in three soils, five croppings with the butyl compound gave results comparable to three with dinitro-*o-cresol*. In the Yolo clay loam even nine crops failed to bring down the toxicity to a value comparable with that for the second cropping with dinitro-*o-cresol*.

The graphs indicate that the Sierra and Yolo fine sandy loams may be placed in a high-toxicity group; Yolo adobe clay, Hanford fine sandy loam, and Yolo clay loam in an intermediate-toxicity group; and Stockton adobe clay, Egbert loam, and Aiken clay loam in a low-toxicity group. This is quite similar to the grouping for the soils treated with dinitro-*o*-cresol (Crafts, 1945). It does not follow strictly a grouping based on textural grade nor one based on fertility; evidently the toxicity of the dinitro-substituted phenols is a more complex function than those of arsenic and chlorate.

Although in a few instances the differences in toxicity between runs were not distinct, in most cases toxicity decreased in a regular order with successive cropping. This indicated that decomposition of the dinitro compound was occurring. As with dinitro-*o*-cresol, this decomposition seemed to stimulate production in the soil at concentration levels that had been toxic to previous crops. Crop number seven showed stimulation in all eight soils.

DISCUSSION

Residual Toxicity. It is apparent that, like dinitro-*o*-cresol, dinitro-*o*-*sec*-butyl phenol compounds could never accumulate in soils in amounts dangerous to crops as a result of normal selective or general contact spraying. For example, to sterilize an acre-foot of soil, weighing roughly 3,600,000 pounds, would require 40 p.p.m. (about 140 pounds of chemical) for the light textures, 100 p.p.m. (about 360 pounds) for the medium group, and 140 p.p.m. (about 500 pounds) for the heavy soils. On the basis of an acre-inch, the corresponding values would be 12.7 pounds, 30.0 pounds, and 41.7 pounds respectively. Since

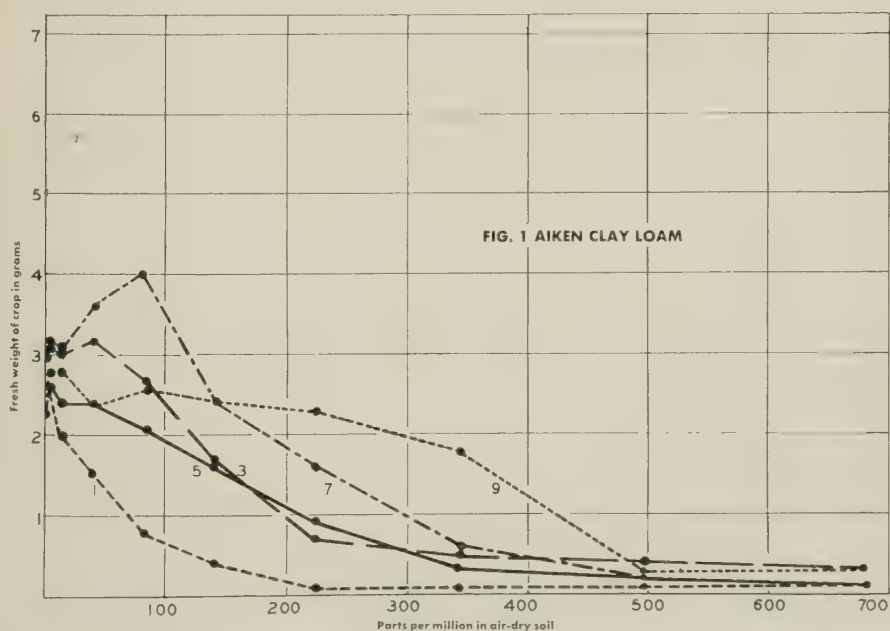


Fig. 1. Toxicity of ammonium dinitro-*o*-*sec*-butylate in 8 California soils to oats as shown by fresh weight.

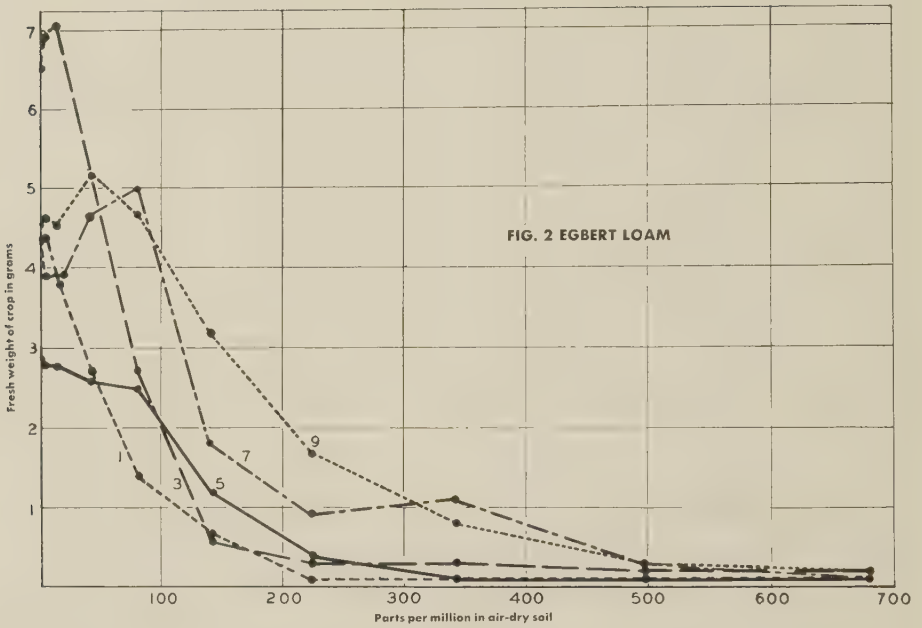


Fig. 2. Toxicity of ammonium dinitro-*o*-sec-butylate in 8 California soils to oats as shown by fresh weight.

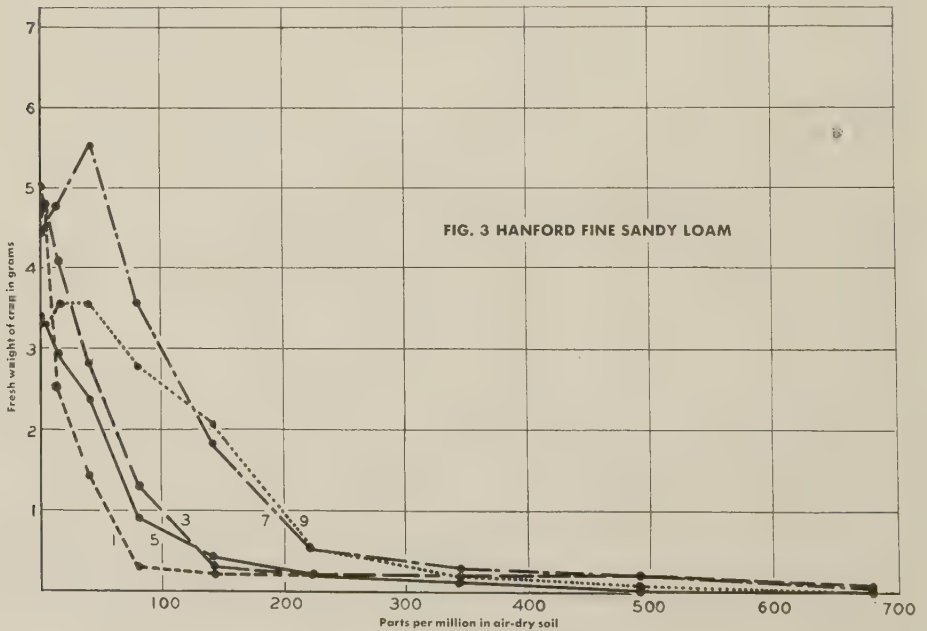


Fig. 3. Toxicity of ammonium dinitro-*o*-sec-butylate in 8 California soils to oats as shown by fresh weight.

selective weed control seldom requires more than one pound of this type of chemical per acre, much of which is absorbed by the weeds, breakdown should normally destroy many times as much as would be needed. On the other hand, to sterilize soils by means of dinitro-*o*-sec-butyl phenol would be out of the question at the present price of this compound.

Tests with Sinox have proved it to be hazardous as a pre-emergence spray. Being readily water-soluble, this chemical may be highly concentrated in a shallow layer of topsoil when light showers follow the spray treatment. Water-soluble compounds of dinitro-*o*-sec-butyl phenol are even more toxic in the topsoil, and they break down at a slower rate. Hence they cannot be used safely in pre-emergence treatments on tender crops.

Recently dinitro herbicides have been used at somewhat higher rates as pre-emergence treatments in cotton, corn, soy beans, and other crops having large vigorous seedlings. Although the crop seedlings are not injured, it seems possible that the herbicide, in the quantities required, might accumulate and eventually give trouble. This might be true in sandy soils underlaid with soil of heavier texture, for once the chemical is leached into the cooler B horizon of the soil, its breakdown would be considerably retarded.

The parent substituted phenols are relatively insoluble in water; their use as fortifying agents in pre-emergence oil spraying should be less hazardous. Preliminary tests in the greenhouse indicate this to be true, but many trials in the field will have to be made before such a procedure can be recommended.

Stimulation. One aspect of the use of dinitro herbicides which is of economic importance is the possible stimulation of crops. Very often cereal crops

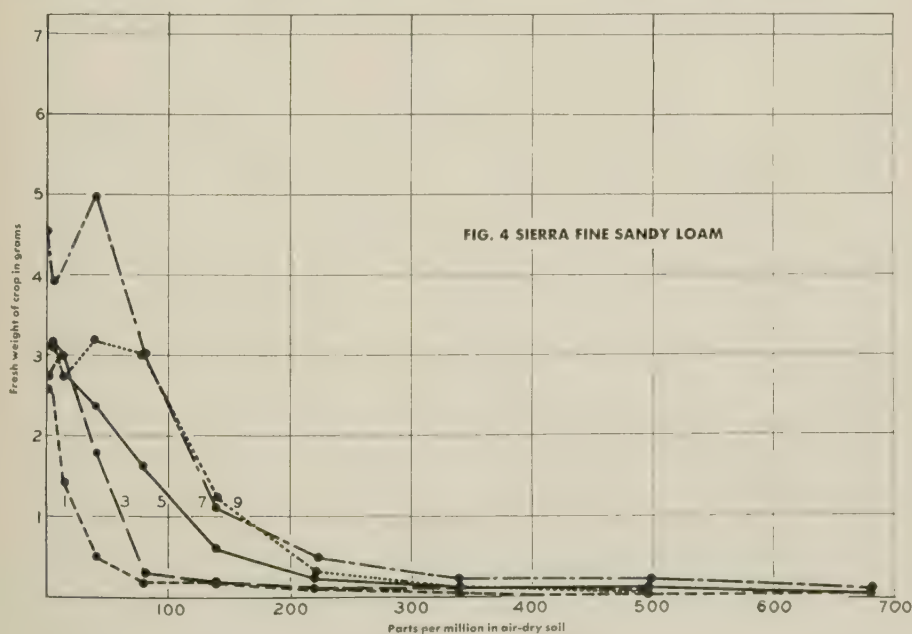


Fig. 4. Toxicity of ammonium dinitro-*o*-sec-butylate in 8 California soils to oats as shown by fresh weight.

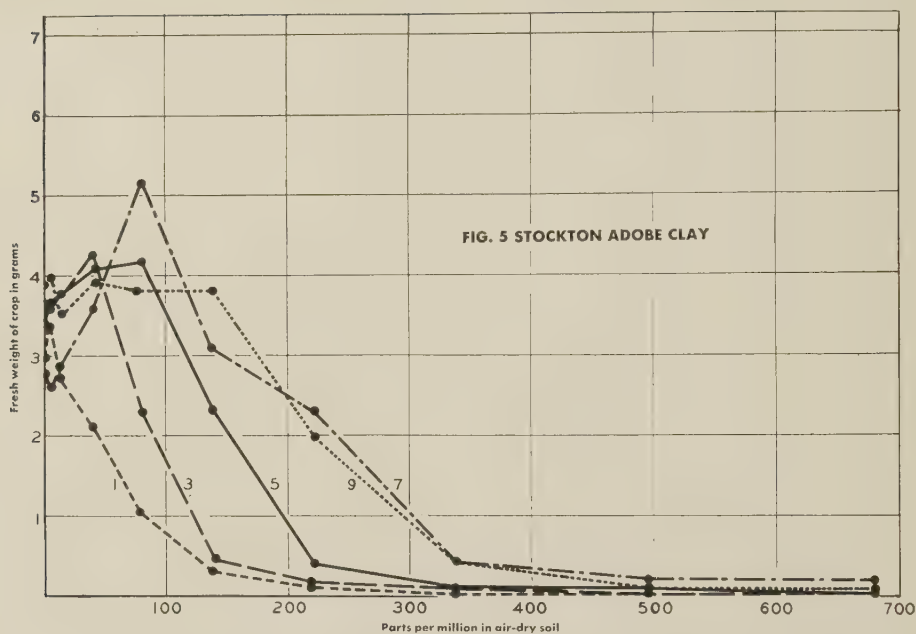


Fig. 5. Toxicity of ammonium dinitro-*o*-sec-butylate in 8 California soils to oats as shown by fresh weight.

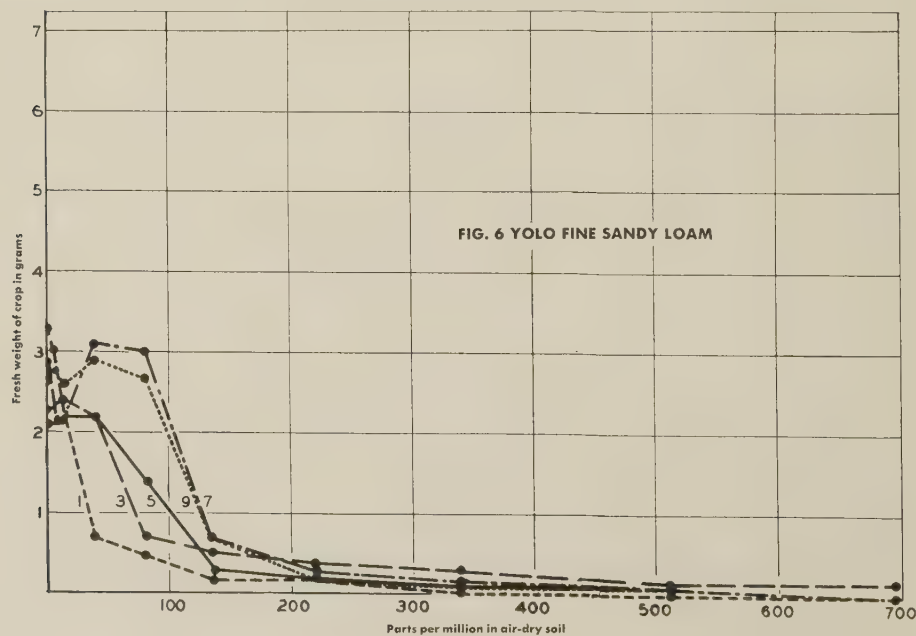


Fig. 6. Toxicity of ammonium dinitro-*o*-sec-butylate in 8 California soils to oats as shown by fresh weight.

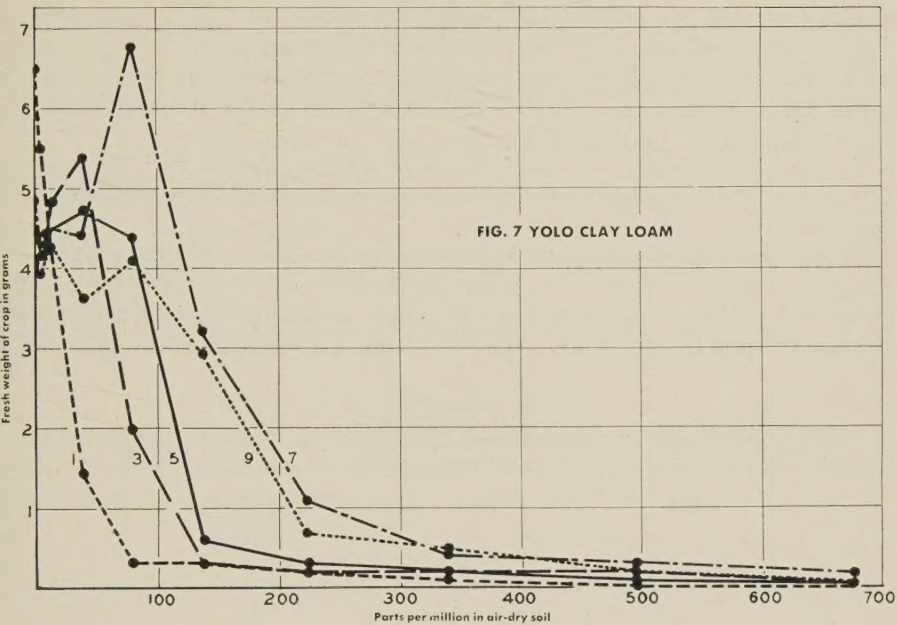


Fig. 7. Toxicity of ammonium dinitro-*o*-sec-butylate in 8 California soils to oats as shown by fresh weight.

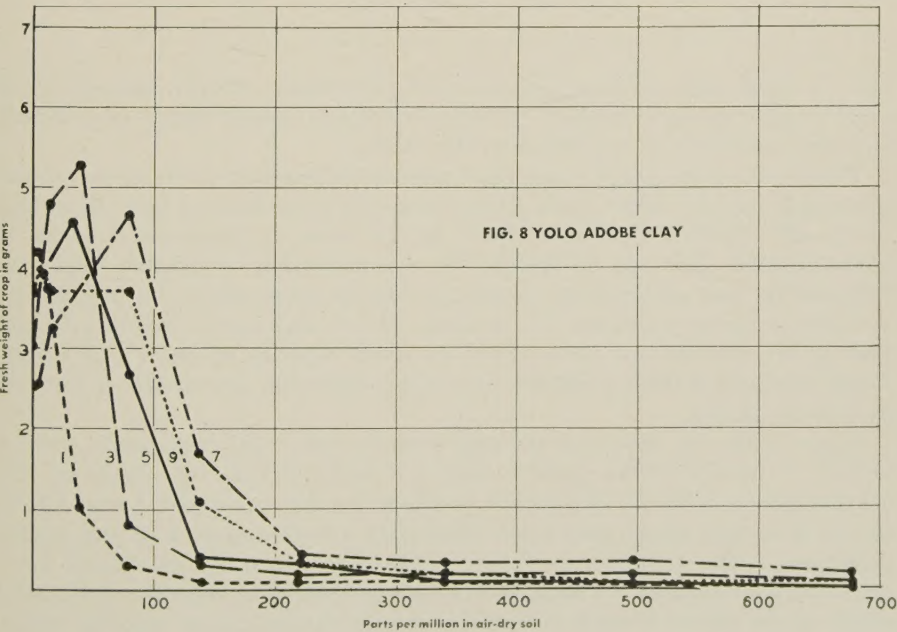


Fig. 8. Toxicity of ammonium dinitro-*o*-sec-butylate in 8 California soils to oats as shown by fresh weight.

sprayed with dinitro selectives are noticeably greener and more vigorous than nearby unsprayed crops. In fact, where plot tests are made by spraying alternate strips through a field, direct comparison shows such stimulation even in areas where, because of a complete lack of weeds in certain parts of the field, weed competition is not a factor.

In the data on toxicity in soils, this stimulating effect is very prominent. Table 1 lists the cases in which crops in treated soils exceeded those in untreated.

Aiken clay loam had cultures exceeding the checks in yield in eight out of nine runs; Egbert loam in seven runs; Hanford fine sandy loam in seven runs; Sierra fine sandy loam in six runs; Stockton adobe clay in eight runs; Yolo fine sandy loam in eight runs; Yolo clay loam in seven runs; and Yolo adobe

TABLE 1
THE NUMBER OF CULTURES OF TREATED SOILS THAT EXCEEDED
IN YIELD THE UNTREATED CONTROL FOR EACH RUN

Run number	Number of soils	Number of cultures
1.....	1	1
2.....	6	14
3.....	8	16
4.....	7	17
5.....	6	14
6.....	7	15
7.....	8	19
8.....	8	20
9.....	8	14

clay in eight runs. Although, in some of these cases, natural variability in yield might explain these high-yielding cultures, it seems highly improbable that they could all be explained on this basis.

These studies on dinitro-*o*-sec-butyl phenol add one more instance to several previously noted (Crafts, 1945, 1948) where the breakdown of toxic chemicals in the soil results in increased yield. In the cases of chlorate and borax, it seems possible that loss of toxicity by decomposition or fixation might be followed by base replacement, making available bases which the crop plants are able to use as nutrients. In the cases where compounds high in nitrogen such as thiocyanate and Ammate are involved, it seems probable that breakdown results in making available nitrogen compounds in sufficient quantities to nourish plants.

Where nitro- or chloro-substituted phenols and 2,4-D compounds are involved, it hardly seems possible that a direct nutrition of plants by the compounds or their decomposition products can be concerned, because they are used in such small quantities. That they are decomposed by soil microorganisms seems probable, for Zobell (1946) has shown that in the soil there are organisms capable of breaking down many such chemicals. The systematic study of the effects of such breakdown should furnish much valuable information relative not only to the use of herbicides in pest control but possibly also to plant nutrition and crop production.

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